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(54) MODIFIED POLYMERS

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The invention relates to a process for the preparation of a modified hydrocarbon polymer by treating the polymer with 0.001-20% by weight, based on the polymer, of an organic sulphonyl azide at a temperature of between 115°C and 250°C.

It is known [illegible] hydrocarbon polymers including cis-1,4 polyisoprene, polybutadiene and styrene-butadiene rubber, but particularly polypropylene and polyisobutylene, can be modified by heating with a monosulphonyl azide having the formula RSO_2N_3, wherein R represents an organic radical. As modifying agent m-carboxy benzene sulphonyl azide (i.e. 3-azido sulphonyl benzoic acid) may be used. The amount of azide used may vary from 0.001 to 20% by weight, based on the polymer to be modified. The sulphonyl azide may be admixed with the polymer in the solid state by means of a conventional rubber mill or in the form of a solution. The modification process is carried out by heating the resulting mixture to a temperature at which the sulphonyl azide decomposes, which temperature may be from 90°C to 300°C. For example, polypropylene is modified by blending it with 2%, based on the weight of the polymer, of 3-pyridine sulphonyl azide and heating the resulting mixture for 2 hours at 150°C. The object of the known method of modification is to prepare products having an improved dyeability, emulsifiability and adhesion to other materials.

It has been found that hydrocarbon polymers are improved also in different respects (e.g. with respect to the green strength) by using as sulphonyl azide a silylester of an organic sulphonyl azide with at least one carboxyl group.

Now, in accordance with the invention a process is provided, which comprises adding to a hydrocarbon polymer 0.001 - 20% by weight - based on the polymer - of a silylester of an organic sulphonyl azide with at least one carboxyl group, then hydrolyzing the silylester and heating the mixture at a temperature of between 115°C and 250°C. The silylesters are new compounds. The invention also relates to silylesters of organic sulphonyl azides with at least one carboxyl group and a process of preparing such esters.

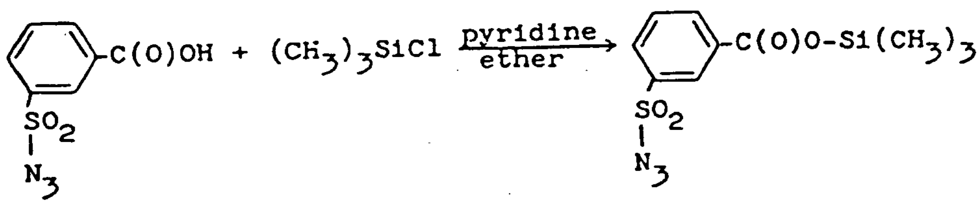
The silylester should be admixed with the polymer at a temperature which is below the temperature at which the ester decomposes. It is preferred that the silylester is admixed with the polymer at a temperature below 130°C, particularly below 120°C. The addition of the silylester to the polymer at a temperature below 130°C is called hereinafter briefly "step A". The heating of the mixture at a temperature of between 115°C and 250°C is called hereinafter briefly "step B".

The silylesters of sulphonyl azides with at least one carboxyl group to be used according to the invention may have more than one azidosulphonyl group, but esters containing only one azidosulphonyl group are preferred. The silylesters may be represented by the general formula $(N_3SO_2)_m$-A-$(C(O)OR)_n$, wherein A is an organic group, for example a phenylene group, R is hydrogen or a silyl group, and m and n represent integers from 1 to 3, preferably 1, at least one R being a silyl group (-$SiH_xR'_y$, wherein R' is an organic group, x is 1, preferably 0, and y is 2 or 3, preferably 3, so that x + y = 3).

The silylesters may be derived from aliphatic sulphonyl azides containing at least one carboxyl group, such as the 4-azidosulphonyl butyric acid trimethyl silyl-ester. Preference is given, however, to silylesters of aromatic azidosulphonyl carboxy compounds having the above formula, in which A represents an aromatic group, such as a phenylene, tolylene or a naphthalene group. The silyl-esters may, for example, be derived from 3-azidosulphonyl benzoic acid, 3-azidosulphonyl-6-hydroxy benzoic acid, 3-azidosulphonyl-6-chlorobenzoic acid, 4-azidosulphonyl-phenoxy acetic acid, 4-azidosulphonyl benzene-1,2-di-carboxylic acid, 5-azidosulphonyl-naphthalene-1-carboxylic acid, 3-azidosulphonyl-4-neopentyl benzoic acid and 3-azidosulphonyl-4-ethyl benzoic acid.

Good results are obtained with 3-azidosulphonyl benzoic acid trimethyl silylester.

The esters can be prepared by silylation of azidosulphonyl carboxy compounds. By silylation is generally meant the addition of an organosilyl group $(-SiH_{0-1}R'_{3-2})$, in particular a trimethyl silyl group, to organic compounds. Known silylating agents are, for example, hexamethyl disilazane, N-trimethyl silyl dimethyl amine, bis(trimethylsilyl)acetamide, bis(trimethylsilyl)trifluoro acetamide, dimethyl chlorosilane, tetramethyl disilazane, bromomethyl dimethyl chlorosilane, chloromethyl dimethyl chlorosilane, bis(chloromethyl)tetramethyl disilazane and N-trimethyl silyl acetamide. Trimethyl chlorosilane is preferred, a tertiary amine, such as triethyl amine or pyridine, being generally also present to bind the HCl split off. The reaction proceeds, for example, according to the following reaction scheme:



Examples of azidosulphonyl carboxy compounds which can be silylated according to the invention have been mentioned hereinbefore.

Suitable conditions for the silylation reaction are: approximately stoichiometric (equimolar) ratios between silylating agent and carboxyl groups of the azidosulphonyl compound; the tertiary amine in a quantity which is approximately equivalent to the quantity of any hydrogen chloride split off; reaction temperatures of between -55°C and 110°C, preferably between 5°C and 80°C; an anhydrous reaction medium; as solvents, for example, toluene, xylene, diethyl ether or carbon disulphide. Since the reaction is exothermic, it is desirable for the reaction temperature to be maintained at the desired level by cooling. The precipitated amine/HCl salt may be filtered off after completion of the reaction and the solvent may be distilled off. If desired, it is also possible to use the silylester solution as such.

When used in the modification of hydrocarbon polymers the silylester is preferably in a solution containing 0.001-20% by weight (based on polymer) of the silylester. A quantity of 0.01-5% by weight, in particular 0.05-0.5% by weight, of the silylester is preferred. These preferred quantities are especially used in the modification of a diene polymer as a hydrocarbon polymer. The concentration of the silylester in the solution may vary between 1 and 90% by weight, in particular between 20 and 60% by weight. Suitable solvents for this solution are those mentioned above as used in the preparation of esters. Particularly

suitable solvents for the invention are aliphatic hydrocarbons, such as i-pentane, n-hexane, iso-octane, kerosine, lubricating oil fractions, especially when diene polymers dissolved in aliphatic hydrocarbons are modified. In this case it is also possible simply to dissolve the silylester in the solution of the diene polymer itself; the ester is very easily soluble therein.

The hydrocarbon polymers which can be modified according to the invention, may be saturated or unsaturated, crystalline or amorphous, linear or branched. Examples of suitable starting polymers are polyethylene, polypropylene, copolymers of ethylene and propylene, polystyrene and poly-isobutene.

The invention is particularly important for polymers of conjugated dienes, such as polybutadiene, cis-1,4-polyisoprene and styrene/butadiene random co-polymer. Preferably the silylester is added to a cement, i.e. a solution of the polymer in apolar solvents. The invention can be applied very successfully to isoprene rubbers prepared with a lithium hydrocarbyl or a Ziegler initiator, the LVN (limiting viscosity number) of which is 2-8 dl/g (measured in toluene at 30°C).

It is particularly with polymers of conjugated dienes that modification according to the invention presents great advantages, in particular when a polymer solution is mixed with the silylester solution.

In the first place the amount of energy required for blending is much smaller than when the carboxy-sulphonyl azide compound is blended in the melt with the polymer. Further, however, blending may be effected at a lower temperature. This combined with the fact that no or only a few shear stresses are exercised on the polymer results in no or hardly any polymer degradation taking place.

It has been found that vulcanizable, sulphur-containing compositions based on a conjugated diene polymer modified according to the invention possess substantially improved mechanical properties (green strength). By "vulcanizable composition" is meant the composition in which all the ingredients required or desired for vulcanization are present and which accordingly is ready to be vulcanized. By "sulphur-containing composition" is understood a composition which, based on the polymer, contains at least 0.5% by weight of free sulphur or sulphur-yielding vulcanization accelerator. The contemplated compositions preferably also contain an oxide and/or salt of a divalent metal (such as, for example, zinc oxide, lead oxide, zinc stearate, lead stearate or combinations of the said oxides with stearic acid). Moreover, other additives, in particular reinforcing fillers, may be present, if desired.

If reinforcing fillers are used, the mechanical properties of the vulcanizable compositions have optimum values if all of these fillers and all of the said other

additives mentioned are only blended with the modified diene polymer obtained in st p B - heating at 115-250°C - once this step has been completed, the blending temperature preferably being below 100°C. In some cases it will be preferred, however, that the reinforcing filler is already present during step A - admixing of the silyl-ester with the polymer at a temperature below 130°C - (and hence also during step B). In these cases it is essential, however, that the sulphur is only blended with the modified diene polymer after step B has been completed, because otherwise vulcanization would take place prematurely. Again, it is preferred to use a temperature below 100°C during this blending. As a rule the accelerator is added together with the sulphur. Similarly, oxides and/or salts of divalent metals are preferably only blended with the modified diene polymer after step B has been completed. If the steps A and B have thus been carried out in the presence of a reinforcing filler and some more azide has been used than would suffice if the reinforcing filler had been added after step B, the final vulcanizable compositions still have a favourable green strength.

If desired, a small quantity (for example 1-10 parts by weight per 100 parts by weight of the diene polymer to be modified) of a processing oil may be used together with the reinforcing filler during

step A. It is also possible to carry out step A in the presence of other additives, such as for example anti-oxidants, anti-ozonants, pigments and non-reinforcing fillers, provided that these substances do not react too strongly with the azide or the decomposition product thereof during step A and/or step B. If it is desired to use extender oils, which are usually incorporated in relatively large quantities, they are in general only added on completion of step B.

As explained hereinbefore, the silylester can be blended with solutions of the polymer. It is also possible to blend molten polymer with a silylester solution at a temperature of below 130°C.

According to another method, a solid polymer, for example in the form of a yarn or fabric, can be wetted with the silylester - if it is liquid - or else with a solution of the silylester, so that only the surface is treated. The temperatures used are preferably as low as possible, such as room temperature.

After the hydrocarbon polymer has been contacted with the silylester solution, the ester is hydrolyzed. This may be effected by means of moisture which is already present, for example, in the mixture of dissolved polymer and silylester. In the reaction, which already proceeds at room temperature, an organic azidosulphonyl carboxylic acid is formed, a disiloxane being split off, which acid

has the formula $(N_3SO_2)_m$-A-$(C(O)OH)_n$, wherein A, m and n have the above meaning. In the case of a mixture of dissolved polymer and silylester, it is advantageous to combine the removal of the solvent with the hydrolysis by steam-stripping the mixture. Fabrics and yarns which are impregnated with the silylester (solution) can also be steam-treated to hydrolyze the ester, for example at 105°C, provided that the polymer has still sufficient stability of shape at this temperature.

After hydrolysis the temperature of the polymer, which is mostly still wet, is raised to a value of between 115°C and 250°C (step B). The azidosulphonyl group then reacts with the hydrocarbon polymer, nitrogen being split off. The azidosulphonyl group reacts within a short time at a relatively low temperature with (diene) polymer double bonds still present. At temperatures of below 200°C, preferably between 135°C and 160°C, the reaction with a diene polymer is mostly completed within 15 minutes, such as between 0.5 and 10 minutes. With saturated polymers such as polypropylene, the reaction proceeds slower, for example, 2 days at 115°C, 5 hours at 150°C or more than 15 minutes at 160°C. If desired, step B and the hydrolyzing step may be combined.

EXAMPLE I

To a solution of 3-azidosulphonyl benzoic acid and .1-equivalent of pyridine (based on acid) in dry diethyl ether a quantity of 1.1-equivalent (based on acid) of trimethyl silylchloride was added at room temperature with the exclusion of moisture (nitrogen atmosphere). After 1.5 hours' stirring at room temperature the resultant pyridine/HCl-salt was filtered off with the exclusion of moisture.

The filtrate was concentrated under nitrogen at reduced pressure to evaporate ether, pyridine and trimethyl silylchloride. A colourless oil remained which - according to infrared spectrum analysis - consisted of substantially pure trimethyl silylester of 3-azidosulphonyl benzoic acid. (Any traces of unreacted acid may be removed by incorporating the oil in pentane or hexane and filtering off the acid insoluble therein). The infrared spectrum of the ester was fully identical with the envisaged structure (no OH-absorption, a strong azide absorption at 2119 cm^{-1} and a strong C=O-absorption at 1690 cm^{-1}). As an additional proof of the structure the ester was treated with water at room temperature, and 3-azidosulphonyl benzoic acid was recovered, which is evidenced by (a) the melting point (122-125°C with decomposition), (b) the mixed-melting point with authentic acid (122-125°C with decomposition), and (c) the infrared

spectrum of the hydrolysis' product which was identical with that of pure 3-azidosulphonyl benzoic acid (OH-absorption at 2800-3300 cm^{-1}, C=O-absorption at 1665 cm^{-1} and azido absorption at 2125 cm^{-1}).

The silylester was soluble in pentane, hexane, benzene, amylenes (isopentenes), diethyl ether and chloroform. On the other hand, the acid was insoluble in saturated and unsaturated hydrocarbon solvents.

EXAMPLE II

(a) The starting material was 7% by wt solution of polyisoprene with an LNV of 7.0 dl/g in amylenes substantially consisting of an isopentene/isopentane/n-pentane mixture. To this solution various quantities (see Table) of 50 % by weight solution of the trimethyl silylester of 3-azidosulphonyl benzoic acid were added at 40°C, whereupon the mixture was stirred at this temperature for 0.5 hours. The solvents were subsequently removed by stripping with steam at 100°C for 0.5 hours, whereupon the wet rubber was dried in vacuo at 40°C for 20 hours. The dry rubber was then heated at 150°C for 5 minutes.

(b) From the resultant modified polyisoprene rubbers vulcanizable compositions were then prepared on a Schwabenthan mill at 65°C and a milling time of 18 minutes according to the following recipe:

Polymer	100 parts by weight
HAF carbon black	50 " " "
ZnO	5 " " "
Stearic acid	3 " " "
Flectol H (a)	1 " " "
Santoflex 13 (b)	1 " " "
Dutrex 729 HP (c)	4 " " "
Sulphur	2.25 " " "
Santocure (d)	0.9 " " "

(a) Trade mark for polymerized trimethyldihydroquinoline

(b) Trade mark for N-1,3-dimethyl butyl-N'-phenyl-paraphenylenediamine

(c) Trade mark for an aromatic processing oil

(d) Trade mark for N-cyclohexyl-2-benzothiazole sulphene amide.

The compositions were subsequently heated in a mould at $80^{\circ}C$ for 5 minutes, whereupon the tensile strength and elongation at break at room temperature were determined. The results are shown in the following table.

Experiment	Silylester parts by wt/ 100 parts of polyisoprene	Vulcanizable composition		LVN (dl/g) of modified rubber
		tensile strength kN/sq.m	elongation at break, %	
(a) for comparison	0	157	360	6.8
1)	0.10	920	1040	5.9
2)	0.15	1420	950	6.8
3)	0.20	1420	625	6.8

EXAMPLE III

To 300 litres of an 18% by weight solution of polyisoprene (prepared with sec. butyl lithium as initiator, LVN 6.5 dl/g) in amylenes a quantity of 76 g of the trimethyl silylester of 3-azidosulphonyl benzoic acid, as a 50% by weight solution in amylenes, was added (i.e. 0.2% by weight based on polyisoprene). After 1 hour's stirring the solvent was removed by means of steam (100°C, 0.5 hours). The wet rubber crumbs were fed to a FOMMCO extruder. The temperature of the initial section was 120°C and that of the end section 150°C. (Like all extruders, a FOMMCO extruder is provided with one or more kneading screws. The barrel in which the screws rotate is provided with a number of slits which facilitate the removal of water and solvent. The dried rubber is extruded from the die head of the machine.) From the resultant dry rubber (300 g) a vulcanizable composition was prepared according to the above recipe on a Troester* mill at 65°C (18 minutes).

* Trademark

For comparison the xperiment was repeated without the use of the trimethyl silylester of 3-azidosulphonyl benzoic acid.

Experiment	LVN of modified rubber (dl/g)	Vulcanizable composition	
		tensile strength kN/sq.m)	elongation at break, %
4) with silylester	4.0	1440	1045
(b) without silylester	5.7	245	840

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A pr c ss for preparing a modified hydrocarbon polym r, which c mprises adding to the polymer 0.001-20% by weight - based on the polymer - of a silylester of an rganic sulphonyl azide with at least one carboxyl group, then hydrolyzing the ester and heating the mixture at a temperature of between 115°C and 250°C.

2. A process as claimed in claim 1, in which the silylester is admixed with the polymer at a temperature below 130°C.

3. A process as claimed in claim 1, in which the silylester is admixed with the polymer at a temperature below 120°C.

4. A process as claimed in claim 1, in which use is made of a silylester of the formula $(N_3SO_2)_m$-A-$(C(O)OR)_n$, wherein A is an organic group, R is hydrogen or a silyl group, and m and n represent integers from 1 to 3, at least one R being a silyl group.

5. A process as claimed in claim 4, in which A is an aromatic group.

6. A process as claimed in claim 4 or 5, in which m and n are 1.

7. A process as claimed in claim 4, in which the silylester used is the trimethyl silylester of 3-azido-sulphonyl benzoic acid.

8. A process as claimed in claim 1, 2 or 4, in which the silylester is used as a solution.

9. A process as claimed in claim 1, in which the hydrocarbon polymer is a polymer of a conjugated diene.

10. A process as claimed in claim 9, in which the hydrocarbon polymer is an isoprene rubber with an LVN between 2 and 8 dl/g.

11. A process as claimed in claim 9 or 10, in which the silylester is admixed with a solution of the polymer.

12. A process as claimed in claim 1, 2 or 4, in which the silylest r is used in a quantity of 0.01-5% by w ight (based on the polymer).

13. A process as claimed in claim 1, 2 or 4, in which the silylester is used in a quantity of 0.05-0.5% by weight (based on the polymer).

14. A process as claimed in claim 1, 2 or 4, in which hydrolysis of the silylester is effected by steam-stripping the mixture with simultaneous removal of any solvent present.

15. A process as claimed in claim 9 or 10, in which the mixture is heated at a temperature of between 135°C and 160°C.

16. A modified hydrocarbon polymer whenever obtained by a process as claimed in claim 1, 2 or 4.